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Quarterly Progress Report

Division 8

Solid State

15 October 1964

Prepared under Electronic Systems Division Contract AF 19(628)-500 by

Lincoln Laboratory
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Lexington, Massachusetts

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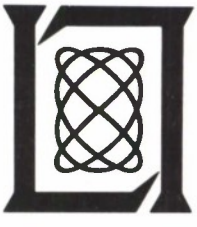

INTRODUCTION

This abbreviated report covers the work of Division 8 from 1 July 1964 through 30 September 1964. A more detailed presentation is covered by the Solid State Research Report for the same period.

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REPORTS BY AUTHORS IN DIVISION 8

15 July through 15 October 1964

PUBLISHED REPORTS

Journal Articles*

JA No.			
2136	Magnetic Properties of a Single Crystal of Manganese Phosphide	E. E. Huber, Jr.† D. H. Ridgley	Phys. Rev. 135, A1033 (1964)
2194	Magnetoreflection Experiments in Graphite	M. S. Dresselhaus J. G. Mavroides	Carbon 1, 263 (1964)
2271	Classical Ground Spin Configurations in the Corundum Lattice	N. Menyuk K. Dwight	J. Phys. Chem. Solids 25, 1031 (1964)
2272	A Cluster Method for Finding Minimum Energy Spin States	D. H. Lyons‡ T. A. Kaplan	J. Phys. Chem. Solids 25, 645 (1964)
2295	Interface-Alloy Epitaxial Heterojunctions	R. H. Rediker S. Stopek J. H. R. Ward	Solid-State Electron. 7, 621 (1964)
2305	Diffused Junction Diodes of PbSe and PbTe	J. F. Butler	J. Electrochem. Soc. 111, 1150 (1964)
2332	Partial Pressures in Equilibrium with Group IV Tellurides. III. Germanium Telluride	R. F. Brebrick	J. Chem. Phys. 41, 1140 (1964)
2335	Band Edge Structure of PbS, PbSe, and PbTe	J. O. Dimmock G. B. Wright	Phys. Rev. 135, A821 (1964)
2344	Galvano-Thermomagnetic Effects in Semiconductors and Semimetals. IV. Mercury Selenide	T. C. Harman	J. Phys. Chem. Solids 25, 931 (1964)
2359	Acoustic Plasma Waves in Semimetals	A. L. McWhorter W. G. May	IBM J. Research Develop. 8, 285 (1964)
2361A	Energy Levels of d^1 Electrons in CaF_2. Evidence of Strong Dynamical Jahn-Teller Distortions	J. R. O'Connor J. H. Chen‡	Appl. Phys. Letters 5, 100 (1964)
2384	Efficiency in a Tetrahedral-Anvil Press as Related to Anvil and Pyrophyllite Size	M. D. Banus S. D. Nye	Rev. Sci. Instr. 35, 1319 (1964)

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JA No.			
2389	Reststrahlen Reflection in HgTe	D. H. Dickey J. G. Mavroides	Solid State Commun. 2, 213 (1964)
2391	Stimulated Raman Emission at 90° to the Ruby Beam	J. H. Dennis P. E. Tannenwald	Appl. Phys. Letters 5, 58 (1964)
2398	Temperature Dependence of Attenuation of 70-Gc/sec Acoustic Waves in Quartz	J. B. Thaxter P. E. Tannenwald	Appl. Phys. Letters 5, 67 (1964)
2405	PbTe Diode Laser	J. F. Butler A. R. Calawa R. J. Phelan, Jr. T. C. Harman A. J. Strauss R. H. Rediker	Appl. Phys. Letters 5, 75 (1964)
2416	Luminescence and Coherent Emission in a Large-Volume Injection Plasma in InSb	I. Melngailis R. J. Phelan, Jr. R. H. Rediker	Appl. Phys. Letters 5, 99 (1964)
2417	Inversion of {111} Surfaces in Single Crystal Regrowth During Interface-Alloying of Intermetallic Compounds	E. D. Hinkley R. H. Rediker M. C. Lavine	Appl. Phys. Letters 5, 110 (1964)
2419	PbSe Diode Laser	J. F. Butler A. R. Calawa R. J. Phelan, Jr. A. J. Strauss R. H. Rediker	Solid State Commun. 2, 301 (1964)
2436	Distribution of Magnetic Moment in Hexagonal Cobalt	R. M. Moon	Phys. Rev. 136, A195 (1964)
2437	Electron-Beam-Pumped GaAs Laser	C. E. Hurwitz R. J. Keyes	Appl. Phys. Letters 5, 139 (1964)
MS No.			
787	Electrical Properties of Praseodymium Oxides	J. M. Honig A. A. Cella J. C. Cornwell	Proc. Third Rare Earth Conference, Clearwater, Florida, 21-24 April 1963
835	Praseodymium – Group V Compounds. I. Vaporization Behavior and Nonstoichiometry of PrP, PrAs, PrSb and PrBi	K. A. Gingerich*	
925	Ferrimagnetic Spiral Configurations in Cobalt Chromite	N. Menyuk K. Dwight A. Wold	J. de Physique 25, 528 (1964)

* Author not at Lincoln Laboratory.

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MS No.			
940	Narrow Band vs Localized d Electrons	J.B. Goodenough	Proc. Buhl International Conference on Materials, Pittsburgh, Pennsylvania, 31 October – 1 November 1963
968	The Fermi Surface of Graphite	M.S. Dresselhaus J.G. Mavroides	IBM J. Research Develop. 8, 262 (1964)

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UNPUBLISHED REPORTS

Journal Articles

JA No.			
2374	Aspherical Spin-Density in S-State Cations	T.A. Kaplan	Accepted by Phys. Rev.
2380A	Optical deHaas-Shubnikov Effect in Antimony	M.S. Dresselhaus J.G. Mavroides	Accepted by Solid State Commun.
2390	Electrochemical Dember Effect in Semiconductors	W.W. Harvey* M.C. Finn	Accepted by Surface Sci.
2392	Single Crystal Growth of Transition Metal Oxides	W. Kunnmann A. Ferretti R.J. Arnott D.B. Rogers	Accepted by J. Phys. Chem. Solids
2394	The Band Gap of Boron Phosphide	R.I. Stearns*	Accepted by J. Appl. Phys.
2412	Peritectic Reaction in the Superconductor Nb_3Sn	F.J. Bachner H.C. Gatos M.D. Banus	Accepted by Metallurgical Trans., AIME
2413A	Band Structure of HgTe and HgTe-CdTe Alloys	T.C. Harman W.H. Kleiner A.J. Strauss G.B. Wright J.G. Mavroides J.M. Honig D.H. Dickey	Accepted by Solid State Commun.
2418	Semiconductor Injection Laser	R.H. Rediker	Accepted by 1965 McGraw-Hill Yearbook of Science and Technology
2446	Electromagnetic Mode Mixing in Nonlinear Media	R.H. Kingston A.L. McWhorter	Accepted by Proc. IEEE
2452	Elastic Constants of HgTe	J.G. Mavroides D.F. Kolesar	Accepted by Solid State Commun.

* Author not at Lincoln Laboratory.

Unpublished Journal Articles (Continued)

MS No.			
989	The Phase Transition Region of $PrO_{1.5}$	D. S. Chapin M. C. Finn J. M. Honig	Accepted by Proc. Fourth Rare Earth Conference, Phoenix, Arizona, 22-25 April 1964
1002	Galvano-Thermomagnetic Phenomena in Bismuth	T. C. Harman J. M. Honig B. M. Tarmy	Accepted by Proc. 1964 International Conference on Physics of Semiconductors, Paris, 19-24 July 1964
1131	Electrical Properties of Interface-Alloyed Heterojunctions	R. H. Rediker S. Stopek E. D. Hinkley	Accepted by Metallurgical Trans., AIME

Meeting Speeches*

MS No.			
983B	Stoichiometry of Electronic Materials	A. J. Strauss	Seminar, Sprague Electric Company, North Adams, Massachusetts, 18 September 1964
1009	Magnetic Properties of V^{3+} Ions in Cubic Spinels	K. Dwight N. Menyuk D. B. Rogers A. Wold	1964 International Conference on Magnetism, Nottingham, England, 7-11 September 1964
1014	Spin Quenching in the System $MnAs_{1-x}P_x$ and $MnAs_{1-y}Sb_y$	J. B. Goodenough D. H. Ridgley W. A. Newman	
1010A	On the Symmetry of Spin Configurations in Magnetic Crystals	J. O. Dimmock	Sagamore Conference on Charge and Spin Density, Sagamore, New York, 18-21 August 1964
1011	Injection Luminescence in InAs Diodes	I. Melngailis	Symposium on Radiative Recombination in Semiconductors, Paris, 27-28 July 1964
1013	Injection Luminescence and Laser Action in InSb	R. J. Phelan, Jr. R. H. Rediker	
1034	The Mass Spectrographic Analysis of Powdered Samples	E. B. Owens	ASTM Mass Spectrometry Conference, Paris, 14-18 September 1964
1071	Theory and Measurements of Intensity Fluctuations in Optical Masers	C. Freed H. A. Haus†	Fifth Congress International "Tubes pour Hyperfrequences," Paris, 14-18 September 1964
1116	Transition-Metal Oxides with Metallic Conductivity	J. B. Goodenough	Symposium on the Oxy-Compounds of Transition Elements in the Solid State, Bordeaux, France, 24-27 September 1964

* Titles of Meeting Speeches are listed for information only. No copies are available for distribution.

† Author not at Lincoln Laboratory.

Meeting Speeches (Continued)

MS No.			
1117	The Effect of Trivalent Manganese on Ordering in Lithium Spinels	R. J. Arnott D. B. Rogers R. W. Germann	American Crystallographic Association, Bozeman, Montana, 26-31 July 1964
1139	Thermoelectric Properties of Ferromagnetic CrO_2	D. S. Chapin J. A. Kafalas J. M. Honig	American Chemical Society, Chicago, Illinois, 30 August – 4 September 1964
1146	Magneto-Optics	G. B. Wright	Conference on Undergraduate Research in Optical Physics, Southwestern College, Memphis, Tennessee, 10 June 1964
1154	Properties, Generation and Uses of Plasmas at Thermal Equilibrium	T. B. Reed	Gordon Research Conference, Tilton, New Hampshire, 27-31 July 1964
1162	On the Possibility of Producing Stimulated Emission in Optically-Excited GaAs	J. J. Schlickman M. E. Fitzgerald L. J. Coyne R. H. Kingston	Boston Laser Conference, Northeastern University, 5-7 August 1964
1166	Review of Laser Diodes	T. M. Quist	
1178	High Pressure Phenomena in Some Compound Semiconductors	M. D. Banus	Gordon Research Conference, Tilton, New Hampshire, 28 August 1964
1179	Metallurgical Aspects of GaAs-Ge Heterojunctions	R. S. Mroczkowski* M. C. Lavine H. C. Gatos	AIME Electronic Materials Conference, Boston, 31 August – 4 September 1964
1181	Junction Injection Luminescence in Semiconductors	R. H. Rediker	Gordon Research Conference, Tilton, New Hampshire, 25 August 1964
1182	Band Structure of HgTe, CdTe-HgTe Alloys and Related Materials	T. C. Harman	Solid State Seminar, RCA Laboratories, Princeton, New Jersey, 24 September 1964
1185	Generation of Stokes and Anti-Stokes Radiation in Raman Media	H. J. Zeiger	Nonlinear Optics Session, Gordon Conference, Meriden, New Hampshire, 31 August – 4 September 1964
1196	deHaas-vanAlphen Effect in Pyrolytic and Single Crystal Graphite	S. J. Williamson* S. Foner* M. S. Dresselhaus	Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 31 August – 4 September 1964
1199	Semiconductor Devices	R. H. Rediker	Electrical Industries Association Symposium, Bedford, Massachusetts, 23 September 1964

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I. SOLID STATE DEVICE RESEARCH

Laser action in which coherent radiation at 5.2 microns emanates from the bulk of the semiconductor has been obtained from InSb n^+pp^+ diodes in which an electron-hole plasma has been established. Below threshold, injection luminescence was obtained from the entire 400-micron length of the bar-shaped p-type base region to which the n^+ and p^+ contacts had been alloyed. The luminescence results as well as the I-V characteristic of the diodes indicate the formation, under forward bias, of a "large" volume injection plasma in the p-region, as was previously reported for the "madistor." Above threshold, the angular spread of the beam indicates coherent spots of 50 microns measured in the direction of the current. This area is about an order of magnitude larger than has been reported for GaAs and InAs lasers. Large, coherently-emitting areas mean smaller beam angles, and the large radiating volume is better suited for light amplification, higher output powers, and may possibly lead to lower threshold current densities. Thus many of the limitations of laser action, when it is confined to the junction region, may be eliminated in this, the first diode bulk laser.

Laser action has been obtained in PbSe diodes operated at 12°K. The emitted coherent radiation was at 8.5 microns. Thus the wavelength range for diode laser action has been extended beyond the previously reported limit of 6.5 microns for PbTe into the 8- to 14-micron "atmospheric window."

Laser action has been obtained in GaAs at liquid helium temperature by generating electron-hole pairs with a beam of 50-kev electrons. The threshold beam current density was about 1 amp cm^{-2} (beam diameter ~0.5 mm). Assuming that the mean total energy required to produce a pair in GaAs is 5 ev, and neglecting any backscattering of the 50-kev electron beam, this is equivalent to a threshold current density of 10^4 amp cm^{-2} in a diode laser. Backscattering of the beam may reduce this value by as much as 50 percent. "Snooperscope" observation of the sample emission indicates that laser action occurs in filaments along the surface on which the electron beam impinges. The beam diameter, although larger than the 0.21-mm distance between the faces of the Fabry-Perot cavity, was smaller than the 1-mm width in the direction perpendicular to the cavity. By sweeping the beam along this width, different filaments have been preferentially excited. The technique of electron beam pumping will hopefully permit laser action to be obtained in the visible in those wide-bandgap semiconductors in which it is difficult to produce good p-n junctions or in which resistivities are so high that series resistance and consequent heating preclude the use of electrical injection.

A miniature pulsed-laser-diode transmitter has been mounted inside a small copper cylinder $\frac{1}{2}$ inch in diameter and 1 inch long. This transmitter, which consists of a GaAs diode laser, a capacitor, a charging resistor, and a pnpn switching transistor has successfully operated at room temperature with $1\frac{1}{2}$ watts of peak power output for a pulse length of 20 nanoseconds. Miniature versions of the requisite power supply and low-power trigger source are now being

fabricated, and the complete transmitter should be much smaller than a two-cell flashlight. This room-temperature pulsed-laser system should have many applications in radar and other range-finding equipment.

Single-crystal $(In_xGa_{1-x})As$ has been grown by a vapor phase reaction, and diodes have been fabricated from these crystals which lased within the 8750 ± 50-Å range required to pump a Nd^{+3} laser efficiently. In addition, the crystal quality has been improved so that the threshold current densities are now typically 3000 amp cm^{-2} at 77°K, and the power output from these mixed-crystal diodes is essentially the same as that from good GaAs diode lasers.

In order to observe the pattern of infrared radiation from the surface of a diode laser, a sensitive scanning infrared microscope has been constructed. This image converter, which uses a slow mechanical mirror scanning system in conjunction with an InSb photodetector, is able to display, on an oscilloscope, images of sources emitting radiation of wavelengths from the visible to 5.4 microns. Potentiometers mechanically linked to the mirror position yield voltage to drive the x- and y-axes of an oscilloscope, and the output signal from the photodetector suitably amplified by a phase sensitive amplifier is used to modulate the intensity of the oscilloscope trace. A magnification of about 25 times with a resolution of about 40 microns has been achieved for this scanning microscope system.

Inversion of the {111} surface occurs in single-crystal regrowth during interface alloying of intermetallic compounds, if A{111} surfaces are mated to A{111} surfaces or B{111} surfaces are mated to B{111} surfaces. Since A{111} surfaces develop etch pits in oxidizing etchants whereas B{111} surfaces do not, we have used etching studies to detect this diatomic inversion in the recrystallized region of the lower-melting-point semiconductor with respect to the unmelted portion of this semiconductor. The results indicate that the recrystallized region grows as a single crystal which emanates from the surface of the higher-melting-point semiconductor.

The Gunn effect oscillator has been operated CW. All such oscillators have previously operated only on a pulsed basis (~1-μsec pulses) to prevent overheating and burnout of the devices. By careful heat-sinking of a 25-micron thick, 125-micron square 1-ohm-cm GaAs, continuous room-temperature operation was possible with the output predominantly at 5 Gcps but with substantial output at many other frequencies. The 5-Gcps frequency is predicted from the equation originally presented by Gunn. It is now necessary to terminate the oscillator with the proper impedance network so that single-frequency operation can be obtained.

II. LASER RESEARCH

Stimulated Raman emission at 90° to the ruby-laser beam in CS_2 has been obtained, and the threshold has been compared with that in nitrobenzene. With mirrors that reflect ruby-laser wavelengths placed in the Raman cavity (filled with CS_2 or nitrobenzene), a narrow laser-like beam at 6943Å radiates at 90° to the primary laser beam. Presently, etalon photographs are being taken to establish that this is a 90° Brillouin laser, down-shifted by 4.25 Gcps from the pump frequency.

Effects of enhancement of stimulated Raman emission by a cavity set at angles other than 0° and 90° to the ruby-laser direction have been observed. The intensity of the anti-Stokes

radiation AS_1 still peaks at the usual phase-matching angle but is optimized when the cavity angle is at the phase-matching angle for S_1.

For a variety of solids and liquids, data have been obtained on the number of stimulated Stokes, anti-Stokes, and multiple-scattering lines that are achievable with a particular ruby laser.

A study has been made of the time, pressure, and wavelength characteristics of the afterglow in a ruby-laser-created breakdown in several gases. Volume electron-ion recombination, and not diffusion, appears to be the dominant loss mechanism of electrons in argon and hydrogen. An argon-afterglow electron temperature of about 5300°K was estimated from the ratio of spectral line intensities, and the electron density of 2.5×10^{18} cm^{-3} was measured from Stark-broadened line widths. There is only a small pressure dependence of the characteristic time of decay of the afterglow.

Perturbation of the refractive index of absorbing media due to the propagation of a 1.06-micron glass laser has been observed in a Mach-Zehnder interferometer. The observed changes of index are consistent with the estimated energy deposition, the known temperature coefficient of the index, and the heat capacity of each medium. The interferometer is illuminated by a very short pulse from an argon laser at varying times after the start of the long-duration glass-laser emission. The index changes in the gas deviated the interferometer rays by almost a milliradian, and the considerable turbulence in the liquid obliterated the interference fringes.

III. MATERIALS RESEARCH

An electric furnace has been developed for heating samples to 2400°C in oxidizing atmospheres, as well as in neutral or reducing atmospheres. The furnace employs a tantalum split-tube heating element, operated in argon, which is isolated from the sample and sample atmosphere by an inner tube of dense zirconia. It has been used successfully for Czochralski growth of sapphire crystals and should also find application in such areas as phase studies, material testing, and diffusion experiments.

Measurements of the Seebeck coefficient and resistivity of polycrystalline CrO_2 prepared by high-pressure synthesis have been extended to liquid helium temperature for samples with compositions of $CrO_{1.994}$ and $CrO_{2.015}$. The stoichiometry of these and other samples was measured by an analytical method which determines the chromium content to an accuracy of about 1 part per 1000. The electrical properties of samples with compositions between $CrO_{1.89}$ and $CrO_{2.02}$ are similar, as expected on the basis of the Goodenough model used to explain the metallic properties and ferromagnetism of CrO_2.

The phase diagram for the pseudo-binary InSb-InTe system has been determined by thermal, x-ray, and metallographic analysis. The system contains a peritectic compound, In_4SbTe_3 (rock-salt structure), which forms a eutectic with InSb. In_4SbTe_3 is the primary phase that crystallizes from the melt between the eutectic point (15 mol % InTe, 508°C) and the peritectic point (40 mol % InTe, 556°C). InTe is the primary stable phase that crystallizes from melts containing more than 40 mol % InTe, but the primary crystallization of In_4SbTe_3 as an unstable phase has been observed for melts containing between 40 and 75 mol % InTe.

Samples of In_4SbTe_3 prepared at atmospheric pressure or below do not exhibit superconductivity down to 1.3°K, the lowest temperature investigated. Samples prepared at high pressure (37 kbar) become superconducting at about 1.5°K, although x-ray diffraction measurements indicate no difference in structure or lattice constant between the low- and high-pressure forms.

Superconductivity measurements have been made on $InSb_{II} - \beta$-Sn alloy samples annealed under pressure (37 kbar) for 20 to 40 hours. Each sample, regardless of composition, exhibits only one superconducting transition, whereas in earlier experiments transitions at two different temperatures were observed in samples containing 0.2- to 0.4-atom-fraction tin which had been annealed for only one hour under pressure. It is concluded that $InSb_{II}$ and β-Sn, which have the same tetragonal structure, form solid solutions in all proportions, if sufficient time is allowed for equilibrium to be reached. The superconducting transition temperature has a maximum value of about 5°K at 0.5-atom-fraction tin, compared with transition temperatures of 2.1° and 3.7°K for $InSb_{II}$ and β-Sn, respectively.

IV. BAND STRUCTURE AND SPECTROSCOPY OF SOLIDS

The experimental investigation of the energy bands in antimony is continuing. Two new sets of oscillations have been observed in the magnetoreflectivity. In contrast to the previously observed deHaas-Shubnikov magneto-oscillations for which the magnetic field associated with a particular oscillation is independent of photon energy, the present phenomenon is strongly frequency dependent and is associated with interband transitions across two different energy gaps. The oscillations are more readily observed when appropriately polarized light is used for the various crystallographic directions. It is believed that these interband transitions can resolve some puzzling features of earlier measurements on the magnetoplasma and optical deHaas-Shubnikov effects.

By using the energy band parameters in graphite obtained from the magnetoreflection experiments, the magnetic susceptibility and microwave transmission in graphite are being calculated. So far, calculations of cross-sectional areas of the Fermi surface indicate that the Slonczewski-Weiss model is capable of predicting all the observed periods, including the long period oscillations recently observed by Soule. Calculations of the microwave transmission yield both Alfvén wave and cyclotron resonance behavior.

Previous measurements of the ultraviolet reflectivity of Mg_2Ge have now been complemented with similar measurements in Mg_2Si and Mg_2Sn. The structure in the reflectivity of these II-IV compounds is very similar to materials of the zinc-blende structure. A Kramers-Krönig analysis on the data is presently under way in order to facilitate interpretation in terms of published band-structure calculations.

On the basis of optical, magneto-optical, and transport experiments and theoretical arguments involving symmetry and continuity, a model has been proposed for the band structure of HgTe and $Cd_xHg_{1-x}Te$ alloys. This model, which is similar to that in gray tin proposed by Groves and Paul except that it includes overlap of the valence and conduction bands, is consistent with the systematics of III-V and II-VI compounds and all available experimental data.

In collaboration with the M. I. T. National Magnet Laboratory and Bell Telephone Laboratories personnel, the nonrelativistic energy bands in gadolinium metal are being calculated. Initial results of the augmented plane-wave calculation indicate marked differences from a free electron model and, in fact, indicate some similarity to the situation in transition metals.

Work on transport problems is continuing. A more general theory of the "collision drag" effect on the ultrasonic absorption in metals has been developed. The theoretical description is based on a transport theory for inhomogeneous driving fields which had been developed previously. The collision drag effect had previously been treated only for special cases.

A formal and systematic treatment of the elastotransport phenomena in one-carrier semiconductors and metals has been completed. Explicit formulas for the piezoeffects due to the electrons have been developed which take into account not only the deformation potential effects, but also the effects of strain on the effective mass tensors, intravalley scattering, and the Fermi level. The formulas are developed in terms of the Fermi-Dirac statistics.

The elastic constants of HgTe have been measured at room temperature by means of the ultrasonic pulse technique. By using the measured values of these constants, a fundamental lattice absorption frequency ω_o, which is in reasonable agreement with far infrared measurements, and a Debye characteristic temperature at absolute zero, $\Theta_o = 105°K$, have been calculated.

A theoretical and experimental study has been made of wave transmission through degenerate hole-electron plasmas, emphasizing weakly transmitted waves which have not previously been examined in detail. Two of these waves, the resonance-damped Alfvén wave and the so-called "branch cut" wave (which is a superposition of single-particle excitations), were studied in bismuth at 4.2°K as a function of magnetic field. At zero magnetic field, the transmitted wave has a phase and group velocity of about 7×10^7 cm sec^{-1} and appears to be due to electron single-particle excitations.

V. MAGNETISM AND RESONANCE

A new high-temperature expansion has been developed which permits calculation of the Curie temperature T_c and provides new insights into the form of the magnetic ordering in the neighborhood of this temperature. It is hoped that this type of investigation will not only provide independent quantitative checks for any exchange-energy formalism, but will also show how to handle the disorder in the spiral components that have been observed below T_c in $CoCr_2O_4$.

Spin resonance can provide important independent information about spin configurations below T_c and is therefore being used to study several chromium spinels. At low temperatures, the spin resonance in $MnCr_2O_4$ and $MnCr_2S_4$ shows satellite structure on the uniform mode resonance. The uniform mode resonance in $CoCr_2S_4$ splits into two resonances at low temperature. It is not yet clear whether the structures observed are related to other modes of the system or are due to powder samples that cause averaging over the anisotropies of the crystals.

Investigation of the breakdown of ligand-field theory has been extended to the thiospinels. It is shown that a consistent interpretation of their magnetic and electric properties requires

the assumption that cationic d-orbitals directed toward nearest-neighbor ligands are transformed via cation-anion covalence into antibonding σ^*-bands. The only exceptions to this generalization may occur when there are four or five unpaired spins per cation.

In order to obtain materials for the investigation of transport properties, work on methods of growing chemically controlled single crystals continues. Vanadium spinels are being grown from fluxes by electrolytic reduction, ReO_3 has been grown by vapor deposition, and suitable fluxes for the growth of YAG and $InVO_4$ host crystals are being investigated.

Several of the rare-earth trifluorides have been prepared and their magnetic susceptibilities have been studied from 4° to 300°K. The materials are characterized by small Weiss constants Θ and values of μ_{eff} close to those expected for free rare-earth ions.

Studies of the effect of Mn^{3+} on the crystal chemistry of lithium spinels have continued. Crystallographic evidence has been obtained to support the idea that, at the critical concentration of Mn^{3+} for the destruction of long-range ordering of Li^+ on the B-sites, there is also a discontinuous change in the distribution of Li^+ ions over the A- and B-sites.

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